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NOVEL ELECTRODES FOR A HYDROGEN-BROMINE BATTERY

SBIR 1984 Phase II

Final Report

SBIR 10.01-7270

NASA Contract No. NAS3-24878

August, 1988

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Prepared by

J.A. Kosek, C.C. Cropley, J. Forchione and A.B. LaConti

GINER, INC.
14 Spring Street
Waltham, MA 02254-9147

Prepared for

NASA-LEWIS RESEARCH CENTER
Cleveland, OH 44135

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A.B. LaConti, Ph.D.
Principal Investigator

ABSTRACT

Advanced electrocatalyst systems for use in a hydrogen-bromine battery were identified. A platinum-rich, low temperature, heat-treated, supported platinum alloy was selected for use as the hydrogen electrocatalyst, while a high surface area amorphous carbon black was selected for use as the bromine electrocatalyst. Full cell testing, implementing the use of an improved flow-by liquid electrode structure, yielded round-trip voltage efficiencies of as high as 78% at room temperature and pressure. Recommendations are given for future research in this area.

ACKNOWLEDGMENT

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1.0 EXECUTIVE SUMMARY

1.1 Objective

The overall objective of NASA Contract NAS3-24878, was the optimization, in terms of stability and performance, of hydrogen and bromine electrocatalysts and electrodes, which could be utilized in a hydrogen-bromine battery. The approach chosen was mainly experimental in nature. Hydrogen and bromine electrocatalysts were prepared, characterized separately and the most promising candidates evaluated under full cell conditions.

1.2 Hydrogen Electrocatalysts

Based on prior work in an SBIR Phase I program, a series of platinum alloys was prepared and evaluated. Parameters investigated included effects of heat-treatment temperature and platinum:alloying component ratio. Another series of platinum alloys, using the optimum heat-treatment temperatures and platinum:alloying component ratios from the first series, was then prepared. This time the composition of the alloying component was varied. The result was the selection of two platinum rich alloys, which had either been subjected to a low-temperature heat-treatment, or no heat-treatment, for full cell testing.

Electrocatalysts of a similar platinum: alloy component ratio, only supported on Vulcan XC-72, a high surface area carbon black, were also prepared. Full cell testing of a supported electrocatalyst structure yielded performance identical to that of an unsupported electrocatalyst. This demonstrated that we were able to lower the hydrogen electrocatalyst precious metal content an order of magnitude without sacrificing performance. The supported structure was subse-

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quently impregnated with Nafion ionomer with the goal of increasing electrode ionic accessibility and tolerance to bromine species. Because of the good performance and potential benefit of this structure, it was selected as the hydrogen electrode of choice.

1.3 Bromine Electrocatalysts

The approach chosen for bromine electrocatalyst optimization was the deposition of impervious carbon coatings onto a high surface area carbon black such as Black Pearls 2000 (BP2000) as part of a composite bromine electrode structure. Parameters investigated included the type of coating, the composition of the coating precursor materials, their concentration and heat-treatment temperatures. Physical characterization data such as BET surface area and iodine adsorption number indicated we were successful in at least partially coating the BP2000; electrochemical half-cell testing revealed no difference in the electrocatalytic activity of the materials. Bromine intercalation testing showed the coatings did not significantly improve stability and BP2000 was quite resistant to intercalation. Ultimately, the BP2000 starting material in conjunction with a metal oxide layer and a metal-activated carbon fiber paper, was selected as the bromine electrocatalyst of choice.

1.4 Full Cell Evaluation

Since the hydrogen-bromine battery undergoing development at Giner, Inc. is a regenerative system in which the same electrochemical cell is used for both charge and discharge, the electrodes and overall performance were evaluated in both modes of operation. Evaluations were initially conducted using a three-component cell structure in

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which free standing electrodes were against, but not bonded to a solid polymer electrolyte membrane. Subsequent work utilized a unitized structure in which all electrodes were bonded to the membrane, leading to an improvement in performance. The addition of a layer of "activated" carbon fiber paper in the bromine electrode structure resulted in another performance improvement. Electrical efficiencies, defined as the discharge voltage/charge voltage ratio at 200 mA/cm^2, as high as 78% were observed in testing at ambient temperature and pressure.

2.0 <u>INTRODUCTION</u>

The hydrogen-bromine battery is being evaluated by NASA as a power source suitable for space applications. This battery could also be used on earth for large-scale energy storage in load-leveling applications (1-4). The battery capacity and power level can be established independently and reactants and products stored externally to the electrochemical cell. One proposed configuration of this system utilizes a solid polymer electrolyte membrane, such as Nafion[R]*, as the cell separator/electrolyte. A schematic drawing of the regenerative hydrogen-bromine system, showing both the charge and discharge modes, is shown in **Figure 2-1**.
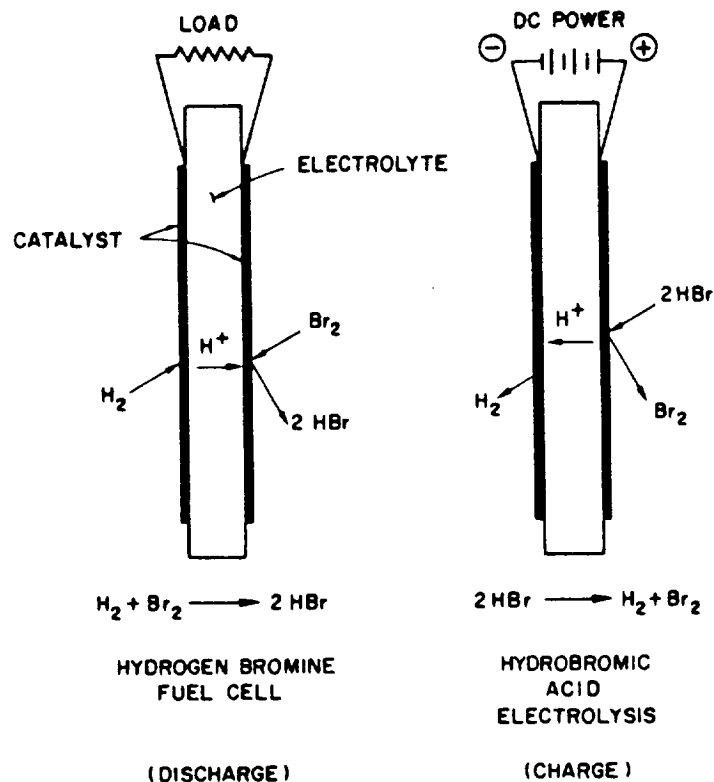
Figure 2-1. Hydrogen/Bromine Regenerative Fuel Cell Cycle

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* Nafion[R] is a registered trademark of the E.I. duPont Corporation

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The hydrogen-bromine cell has several advantages which make it attractive for use: (a) the system has high electric-to-electric voltage efficiency because of fast electrochemical reaction kinetics of both the hydrogen and bromine electrodes; (b) the same electrochemical cell can be used for both charge and discharge operations which would lower the power/weight requirements for a space-based power source; (c) the use of a solid polymer electrolyte membrane allows a high differential pressure to be obtained in the cell; (d) the cell has a high coulombic efficiency because of low parasitic losses due to reactant permeability (estimated to be <3 percent at 25°C (5)); and (e) there are essentially no mass transfer limitations in the cell operation, except at low bromine concentrations, because of the high solubility of bromine in the hydrobromic acid electrolyte.

A major concern of this system which must be resolved is the adsorption of bromide ions on the hydrogen electrode which results in poisoning of the electrode. This problem is caused by the incomplete exclusion of bromine species by presently available commercial solid polymer electrolyte membranes (5,6).

Nafion-type membranes which are utilized as permselective solid polymer electrolytes, would ideally transport only protons (or cations). Thus, under ideal conditions in a hydrogen-bromine battery, the hydrogen electrocatalyst will only be exposed to gaseous and ionic hydrogen. In reality, Nafion membranes do not completely prevent bromide ions from migrating across the membrane and adsorbing on the hydrogen electrode. Similarly, the membrane does not completely exclude other bromine species (Br_2, Br_3^-), which also migrate across the membrane and poison the hydrogen electrode surface.

Some of the transport processes occurring through a solid polymer electrolyte membrane during the discharge mode of operation are shown in **Figure 2-2**. The H^+ ions formed from the oxidation of H_2 gas are transported from anode to cathode along with some water molecules. The number of water molecules electroosmotically transported with each H^+

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ion is a strong function of membrane water content and varies from approximately 3.5-4 H_2O/H^+ at low HBr concentrations (1M) to 0.5-1 H_2O/H^+ at high acid concentrations (8M). There is also some permeability of H_2 through the membrane to the Br_2 side and Br_2 to the H_2 side. Parasitic losses due to Br_2 permeation are approximately 1 to 2% at 200 mA/cm², 25°C (5,6) and decrease with increasing operating current density. The product HBr that forms at the membrane/electrode interface during discharge is concentrated and must be diluted effectively to minimize back migration of Br^- ion which generally increases with increasing Br^- concentration. Also effective dilution of product HBr is necessary since membrane ionic resistance increases with increasing acid concentration as shown in **Figure 2-3** (5).
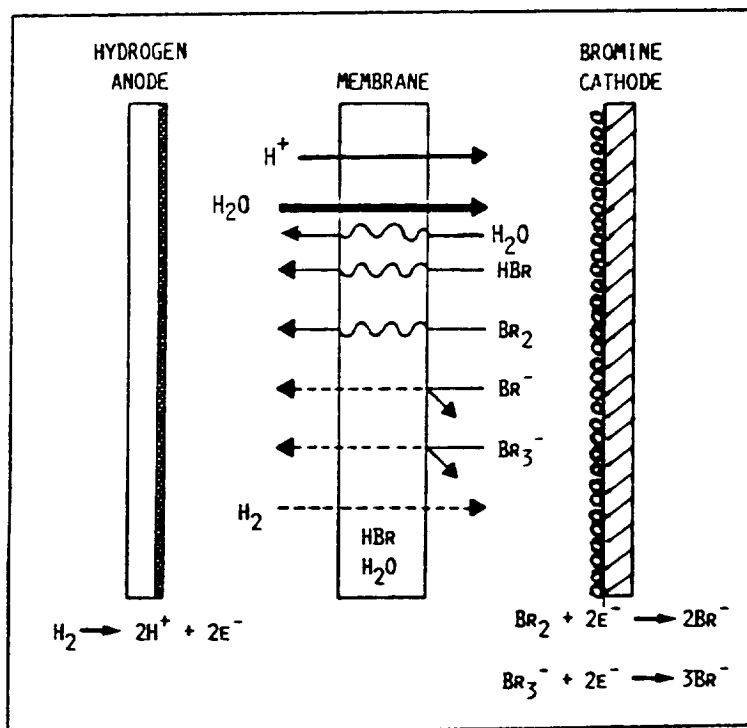
Figure 2-2. Transport Processes Through a Solid Polymer Electrolyte During Discharge Mode of Operation of a Hydrogen-Bromine Cell.

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STATE OF CHARGE (%)
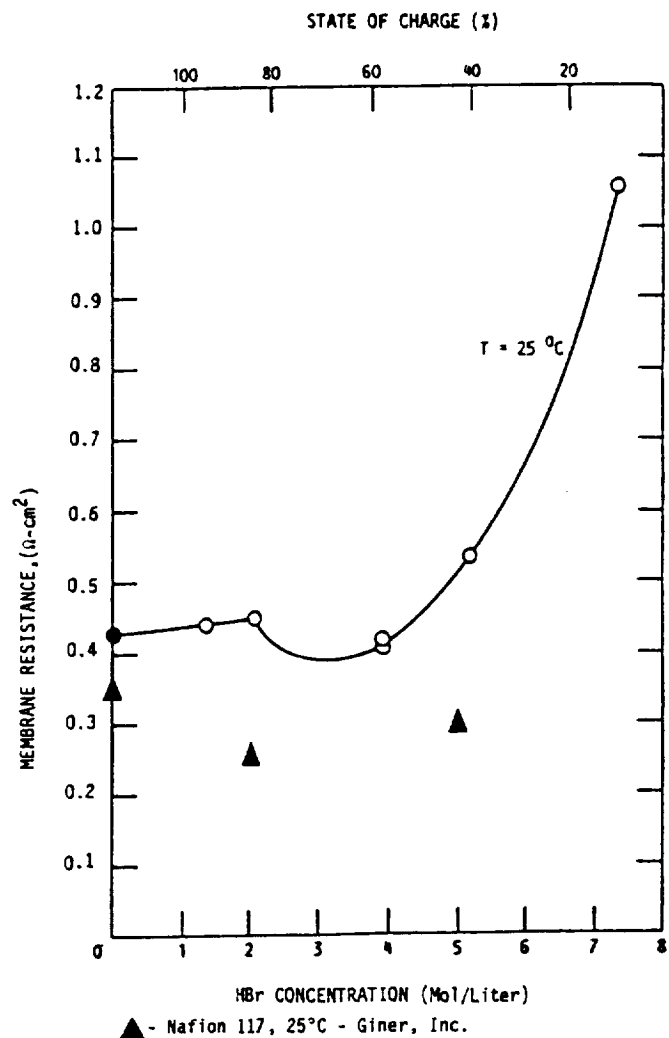
Figure 2-3. Specific Resistance of Nafion-120
            as a Function of HBr Concentration
            (Baldwin, R.S., NASA Technical Memo
            89862, 1987 - Reference 5)

The state-of-the-art hydrogen electrocatalyst, Pt black, is known
to adsorb halide ions, "become poisoned," and render decreased
hydrogen oxidation/reduction activity (7-9). In addition, if allowed
to reach a sufficiently high anodic potential (such as during
deprivation of hydrogen or during a high-rate discharge) the presence
of bromide ion on the Pt black will cause the Pt black to dissolve.
Studies have shown that this dissolution can be minimized by always
maintaining the electrode near the reversible hydrogen potential.
Also, studies conducted in this laboratory under NASA Contract NAS3-
24394 have identified a Pt alloy which has improved tolerance to
bromine/bromide ion adsorption, as compared to Pt black (10).

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Another area of concern of this system is the potential of intercalation compound formation when using a carbon-based bromine electrode. The formation of bromine intercalation compounds with highly ordered graphitic structures is well-known. Over an extended period of time, the formation of intercalation compounds may lead to possible degradation of the bromine electrode structure.

Under NASA Contract NAS3-24878, Giner, Inc. undertook a program to identify solutions to these problems. The objective was the optimization, in terms of stability and performance, of hydrogen and bromine electrocatalysts and electrodes. The approach chosen to address the hydrogen electrocatalyst problem was the preparation and evaluation of platinum alloys, which would have improved tolerance to the presence of bromide ion. The approach chosen for the bromine electrocatalyst was the deposition of impervious coatings on a high surface area carbon black, with a goal of minimizing formation of bromine intercalation compounds. In addition, use of a composite metal oxide/carbon black electrode structure was implemented during full cell operation.

The overall program was mainly experimental in nature. Hydrogen and bromine electrocatalysts were prepared, characterized separately and the most promising candidates then evaluated under full cell conditions. Since the hydrogen-bromine battery being evaluated at Giner, Inc. is a regenerative system in which the same electrochemical cell is used for both charge and discharge (hence a higher power density with respect to two separate cells), the electrodes and overall performance were evaluated in both modes of operation.

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3.0 HYDROGEN ELECTROCATALYST OPTIMIZATION

3.1 Introduction

During this SBIR Phase II program, we have conducted research on the hydrogen electrocatalysts with the goal of optimizing the electrocatalysts identified previously during a Phase I program (1). The following variables were studied during the optimization program: a) composition of alloying component, b) ratio of platinum to alloying component and c) heat-treatment temperature. In addition, we investigated the possibility of preparing hydrogen electrocatalysts in a supported form. That is, a starting material of 10% platinum (by weight) dispersed on a high surface area carbon black was used to form the alloy. Electrocatalysts of this type are used in phosphoric acid fuel cells. A listing of all the platinum alloys prepared during this program, their compositions and designations, is summarized in **Table 3-I.**

TABLE 3-I

HYDROGEN ELECTROCATALYST DESIGNATION

Designation	Expected Composition
G86-1-1	90:10 wt% Pt:Ru (82:/18 atom)
G86-1-2	90:10 atomic % Pt:Ru
G86-1-3	75:25 atomic % Pt:Ru
G86-1-4	50:50 atomic % Pt:Ru
G86-1-5	25:75 atomic % Pt:Ru
G86-1-6	90:10 atomic % Pt:In
G86-1-7	9:5:5 atomic % Pt:Ru:In
G86-1-8	90:10 atomic % Pt:Ir
G86-1-9	90:10 weight % Pt:Ru/Vulcan XC-72
G86-1-10	90:10 atomic % Pt:In/Vulcan XC-72

Three criteria were used to evaluate the various electrocatalysts, compositions and preparation procedures of the finished electrodes. These were: 1) hydrogen adsorption surface area in the presence and absence of bromide ion, 2) polarization performance in a hydrogen oxidation half-cell in the presence and absence of bromide ion, and 3) resistance to corrosion in the presence of bromide ion. Surface area testing by cyclic voltammetry was performed to compare the effect of bromide ion concentration on the hydrogen adsorption area for the various electrocatalysts. Corrosion testing was conducted to determine the relative stability of the electrocatalysts when exposed to 1) high anodic potentials, 2) an acid electrolyte, 2M H_2SO_4 simulating the solid polymer electrolyte, and 3) bromide ion, 1M KBr simulating the permeation of bromine species from the bromine to the hydrogen compartment.

3.2 Catalyst Preparation

The electrocatalysts were prepared by the co-precipitation of platinum and the base metal using a modification of a procedure originally published by Giner, et al. (2). For most preparations, HCHO was used to reduce a mixture of chloroplatinic acid and a salt of the alloying metal. The G86-1-8 preparation used $NaBH_4$ for its greater reducing ability. After filtration and drying, portions of each batch were subjected to heat treatment in an inert atmosphere (N_2) at temperatures ranging from 500°C to 900°C. Binary alloys based on the G86-1-1 electrocatalyst (identified during the Phase I program) were prepared in atomic ratios ranging from 90/10 to 25/75 and were designated G86-1-2 through G86-1-5. Two other binary alloys, G86-1-6 and G86-1-8, were made using a 90/10 atomic ratio while the G86-1-7 ternary alloy was prepared using a 90/5/5 atomic ratio.

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The supported G86-1-9 electrocatalyst* was prepared by blending a dissolved metal salt with 10% Pt/Vulcan XC-72, filtering, drying and heat-treating for one hour at 500°C in a hydrogen atmosphere. The supported G86-1-10 electrocatalyst was prepared by two methods. One method (used to prepare G86-1-10B) was similar to that described above for the G86-1-9 electrocatalyst. For the other method (used to prepare G86-1-10A), the alloying component was precipitated onto 10% Pt/Vulcan using a standard Giner, Inc. procedure for the preparation of high surface area electrocatalysts. Due to their preparation procedures, the G86-1-9 and G86-1-10 electrocatalysts were subjected to a 500°C heat-treatment under hydrogen; they cannot be effectively prepared without heat-treatment. This thermal treatment has generally been found to enhance the stability of the noble metal catalyst material in both unsupported and supported catalyst systems at Giner, Inc.

Prior to use in the full cell, liquid Nafion was used to impregnate the G86-1-9 and G86-1-10 supported electrocatalysts, for increased hydrogen ion accessibility and possible assistance in excluding bromine species. Studies at Giner, Inc. in another program have demonstrated that Nafion impregnation of an electrode, followed by drying/annealing, minimizes chloride ion permeability to the electrode. The annealing step is required and lowers the water content of the ionomer, thus increasing chloride exclusion. Only one annealing temperature was used in these studies.

*Note: This material, originally intended as a 90:10 atomic ratio (Pt rich), was inadvertently prepared with a 90:10 weight ratio (82:18 atomic ratio). In the monthly reports the composition was erroneously listed as a 90:10 atomic ratio.

Samples of catalysts were analyzed by Scanning Electron Microscopy (SEM) for particle size, Energy Dispersive X-Ray Analysis (EDAX) for composition, and X-Ray Diffraction (XRD) to confirm alloy formation. SEM analysis was performed using magnifications up to 50,000X; catalysts examined were the G86-1-2 through -5 including the as-prepared and heat-treated samples. Even at the highest magnification, individual catalyst particles could not be seen. Instead, agglomerations of catalyst particles were visible. Sintering was evident in the 700 and 900°C heat-treated samples, with a loss of fine structure and a smoother catalyst surface visible. The samples examined were prepared in atomic ratios ranging from 90 Pt/10 alloying component to 25/75; EDAX confirmed the presence of the alloying component (qualitatively, not quantitatively). Lattice parameters from XRD data are summarized in **Table 3-II**. Several trends in the data were noted. For a given electrocatalyst, the lattice parameter initially increased, then decreased with increasing heat-treatment temperature. At a given heat-treatment temperature, the lattice parameter decreased with decreasing platinum content; a similar trend has been noted for platinum ternary alloy electrocatalysts fabricated for use as a phosphoric acid fuel cell cathode.

In **Figure 3-1**, lattice parameters of the non-heat-treated G86-1-2 through G86-1-5 alloys have been superimposed on a plot taken from the literature, showing lattice parameters for alloys prepared both as polished sheets and Raney alloys. The decrease in lattice parameter with decreasing Pt concentration is consistent with the published work and the formation of alloys (3).

TABLE 3-II

LATTICE PARAMETERS CALCULATED FROM XRD SPECTRA

Catalyst Designation	Atomic Ratio	Lattice Parameters (Å) at Heat-Treatment Temperatures of				
		None	500°C	700°C	900°C	1100°C
Pt	100:0	3.911	NT	NT	NT	NT
G86-1-2	90:10	3.908	3.915	3.915	3.914	3.908
G86-1-1	82:18	3.903	NT	NT	3.914	NT
G86-1-3	75:25	3.896	3.909	3.908	3.904	3.889
G86-1-4	50:50	3.863	3.885	3.871	3.870	NT
G86-1-5	25:75	3.848	3.852	3.853	NT	NT

NT = Not Tested
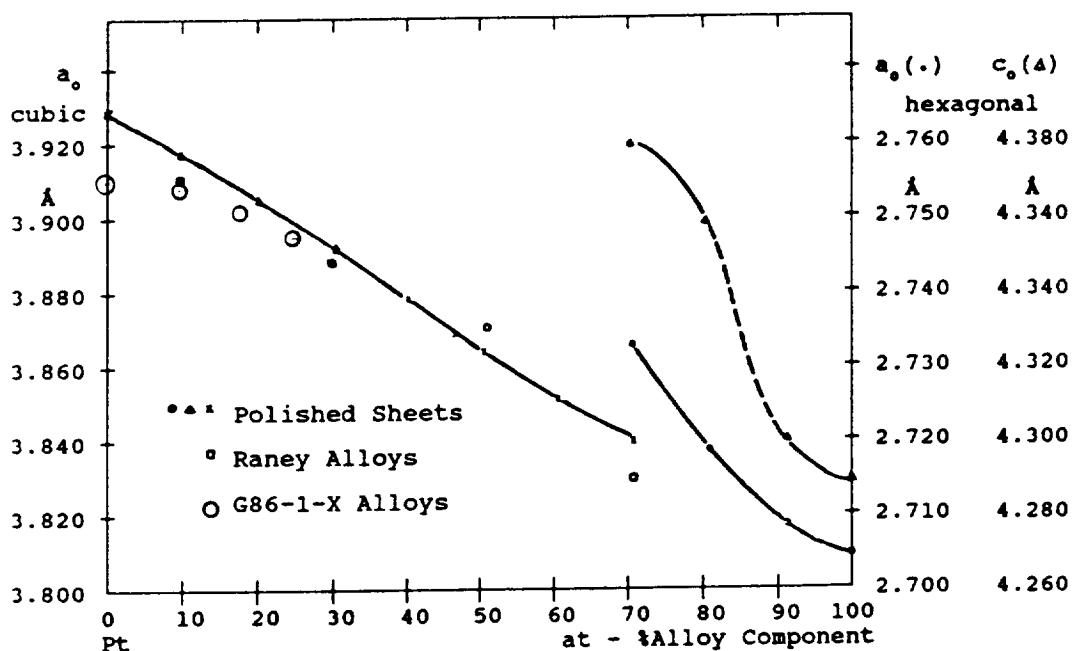
Figure 3-1. Lattice Parameters of Platinum Alloys

3.3 Catalyst Evaluation

3.3.1 Surface Area and Effect of Br_2/Br^-

Gas diffusion electrodes were fabricated from the electrocatalysts with loadings of 7.5 mg/cm^2 plus 5% PTFE binder and sintered at 345°C. Carbon fiber paper was used as a substrate.

Surface areas were determined by cyclic voltammetry; the hydrogen adsorption charge was measured and converted to real surface area using the standard 210 μCoul/cm^2 for Pt. Electrode potentials were scanned between 0 and 900 mV vs. a dynamic hydrogen electrode (DHE) in electrical contact with the sensing electrode by means of a Luggin capillary. Results were not corrected for the effect of a liquid junction potential. Electrochemical surface areas were measured initially in 2M H_2SO_4 and then in the presence of increasing amounts of bromide ion added as KBr to the solution.

Results of the surface area testing for all the electrocatalysts are summarized in **Table 3-III**. The data are presented here as surface areas in m^2/g both in 2M H_2SO_4 (S_0) and 2M H_2SO_4 + 4.5M KBr (S). **Table 3-IV** has the decimal fraction ratios S/S_0 for these pairs.

Initial investigation of the hydrogen electrocatalysts was concentrated on different alloying component ratios and heat-treatment temperatures of the G86-1-1 system. **Figure 3-2** is a plot of S/S_0 values vs. Br$^-$ concentration for Pt black and the various non-heat-treated G86-1-2 through G86-1-5 alloys, all variations of G86-1-1, having the same alloying constituent. It has been demonstrated in the literature that bromide ion adsorption on a smooth platinum surface, for bromide ion concentrations in the range 1×10^{-6} to 1×10^{-3}M will not decrease the area available for hydrogen adsorption (4). Therefore, concentrations below 1×10^{-3}M were not tested here. As

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shown in Figure 3-2, S/S_0 values greater than 1 have been observed for platinum black. It is suspected that during the cycling of the electrode potential, the platinum surface is roughened by a dissolution mechanism, thus increasing the effective surface area of the electrode. The data in Figure 3-2 indicate that the tolerance to Br^- decreases as the Pt content decreases; Pt black has the highest initial surface area (29 m^2/g), and the highest S/S_0 (~0.90) for 2M H_2SO_4 + 4.5M KBr.
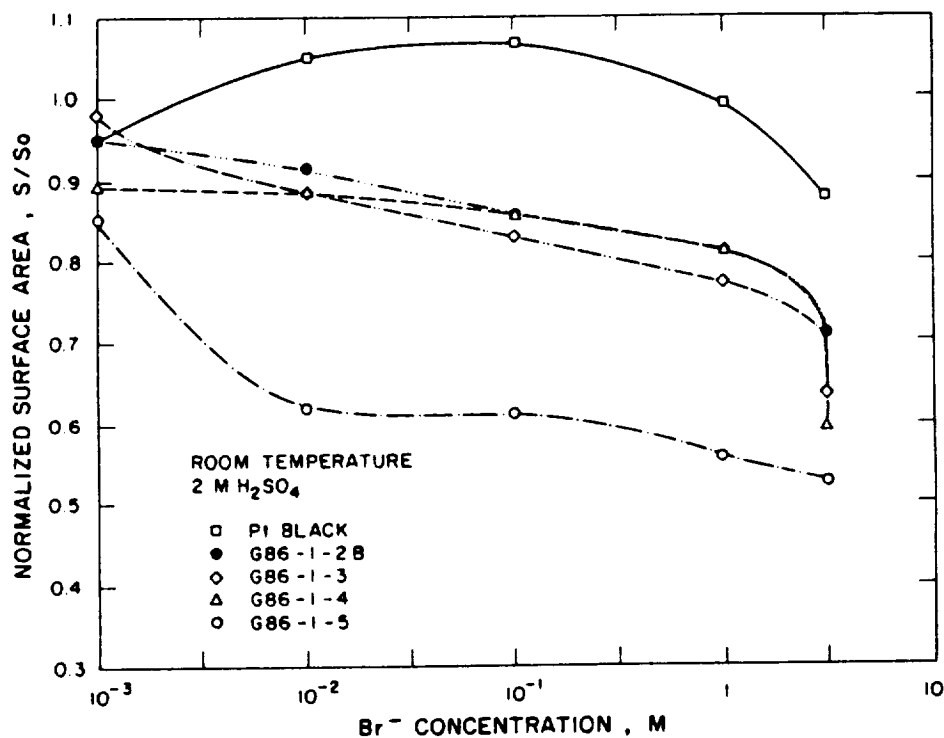
Figure 3-2. Effect of Bromide Ion Adsorption on Electrocatalyst Surface Area

From Tables 3-III and 3-IV, it can be seen that, for all the unsupported alloys tested, the G86-1-6 and G86-1-7 non-heat-treated alloys had the highest surface areas (30 and 33 m^2/g, respectively); the tolerance to Br^- of the -6, -7, -8 catalysts was generally >0.80, better than the -2 through -5 alloys. There is no clear trend with heat-treatment at 500°C vs. non-heat-treatment; the -6 decreased from 0.94 to 0.78 while the -7 increased from 0.80 to 0.93. For heat-treatment above 500°C, surface areas dropped drastically and tolerance generally decreased as well.

The trends are not as clear for the supported electrocatalysts. High surface areas, which were expected, were observed for all materials in the absence of bromide ion. The presence of the Nafion coating lowered the available surface area for two of the supported electrocatalysts, G86-1-9 and G86-1-10A, while increasing the surface area for G86-1-10B. The use of Nafion in the electrode structure may mask some of the electrocatalyst particles, leading to the decrease in surface area. The increase in area observed for G86-1-10B is not completely understood, but appears to be related to the electrocatalyst preparation method. The -10A electrocatalyst was prepared by precipitating the alloying component as a hydrated metal oxide onto the platinized support, while the -10B was prepared by combining the platinized support with a soluble metal salt. The trends in surface areas were noted several times, using different electrodes prepared with different PTFE contents.

The non-Nafion impregnated supported electrocatalysts all exhibit very good tolerance to the presence of bromide ion (S/S_0 values range from 0.90 to 1.05). These values are higher than those observed for the 500°C heat-treated G86-1-2 and G86-1-6 electrocatalysts. The presence of Nafion, however, leads to unusual results. Observed surface areas, in the presence of concentrated bromide ion, are larger

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TABLE 3-III

HYDROGEN SURFACE AREAS

Catalyst	Heat Treatment				Nafion Impregnated (500°C)
	None	500°C	700°C	900°C	
Non-Supported					
Pt	29/26	2.4/1.3		5.2/2.2	
G86-1-2	15/11	10/7.2	8.2/3.4		
G86-1-3	20/13	13/8	7.6/3.4		
G86-1-4	20/12	16/11			
G86-1-5	23/12	14/10			23/15
G86-1-6	30/28	19/15	1.2/1.1		
G86-1-7	33/26	17/16	2.3/1.8		
G86-1-8	18/16	16/15	0.9/0.6		
Supported					
G86-1-9		93/84			70/93
G86-1-10A		73/77			56/79
G86-1-10B		71/65			87/87

Note: First number S_0 (m²/g); no bromide

Second number S (m²/g); saturated KBr

TABLE 3-IV

S/S$_0$ VALUES IN KBr SOLUTION

Catalyst	Heat Treatment				Nafion Impregnated (500°C)
	None	500°C	700°C	900°C	
Non-Supported					
Pt	0.90	0.54			
G86-1-2	0.73	0.72	0.41	0.42	
G86-1-3	0.65	0.62	0.45	0.50	
G86-1-4	0.60	0.69			
G86-1-5	0.52	0.71			0.65
G86-1-6	0.93	0.79	0.92		
G86-1-7	0.79	0.94	0.78		
G86-1-8	0.89	0.94	0.67		
Supported					
G86-1-9		0.90			1.33
G86-1-10A		1.05			1.41
G86-1-10B		0.92			1.00

than the original S_0 values; this is attributed to wetting of the Nafion coating during the course of the experiment, resulting in improved wetting of the electrocatalyst particles. Note the good agreement between the S_0 values for the non-impregnated electrocatalysts and surface areas for the Nafion-impregnated catalysts in the presence of bromide ion. In addition to wetting the Nafion, bromide ion adsorption on the electrocatalyst surface also occurs, as evidenced by changes in the shape of the current-voltage curves. However, as demonstrated with the non-Nafion impregnated electrodes, these materials demonstrated good tolerance to the presence of bromide ion.

3.3.2 Floating Electrode Half-Cell Performance

The hydrogen floating electrode half-cell experiments were performed in order to evaluate the ability of the electrocatalysts to oxidize hydrogen in the absence and presence of bromide ion. In the floating electrode half-cell experiments a 1 cm² disk electrode is held face down on the surface of the electrolyte, 2M H_2SO_4. After deaeration of the cell with N_2, a hydrogen atmosphere is maintained above the electrode. The potential of the electrode (vs. DHE) is adjusted to bring the current to a series of preselected values. The iR correction is determined after the current scan using a current interruption technique with the voltage decay recorded on an oscilloscope and photographed. The data, plotted as overvoltage vs. current, shows the degree of polarization for the hydrogen oxidation reaction on the selected electrode.

A summary of the results for all electrocatalysts tested is presented in **Table 3-V**. In this table the maximum current density (mA/cm²) obtained at an arbitrary polarization overvoltage of 50 mV is presented both in 2M H_2SO_4 and 2M H_2SO_4 + 4.5M KBr. General trends

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indicate that heat-treatment decreases the currents obtained at 50 mV overvoltage. Among the −2 through −5 alloys, −2 non-heat-treated showed the best performance and is closest to pure Pt, suggesting an advantage to the Pt-rich alloys. Among the other alloys (−6, −7, −8), −6 was the best with >1000 mA/cm² at 50 mV overvoltage in 2M H_2SO_4 and 800 mA/cm² in 2M H_2SO_4 + 4.5M KBr. For electrocatalysts heat-treated at >500°C, performance dropped sharply due to a decrease in surface area. The supported electrocatalysts, −9 and −10, showed performance comparable to the pure metal alloys; performance of −9 electrocatalyst even exceeded the current density of −2 in 2M H_2SO_4, a surprising result considering it contains only 10% metal content.

TABLE 3-V

SUMMARY DATA OF H_2 FLOATING ELECTRODE HALF-CELL TESTS
(c.d. in mA/cm² for polarization
of 50 mV in H_2SO_4 and in
H_2SO_4 + Saturated KBr)

Catalyst	Heat Treatment				Nafion Impregnated (500°C)
	None	500°C	700°C	900°C	
Non-Supported					
Pt	900/300[a]	N.D.[b]			
G86-1-2	800/200	300/200	200/100	60/50	
G86-1-3	400/200	200/200	200/100	200/20	
G86-1-4	600/200	300/80			
G86-1-5	400/200	400/200			600/600
G86-1-6	>1000/800	>1000/400	30/15[c]		
G86-1-7	700/80	600/300	48/ND[c]		
G86-1-8	600/140	---	200/100[c]		
Supported					
G86-1-9	---	1000/200			1000/200
G86-1-10A	---	1000/100			800/100
G86-1-10B	---	1000/200			1000/100

a In H_2SO_4/In (H_2SO_4 + Saturated KBr)
b Not Determinable (low currents)
c Second number in H_2SO_4 + 1 x 10^{-3}M KBr

3.3.3 Accelerated Corrosion

In the accelerated corrosion tests 50 mg of electrocatalyst was placed in a closed vial containing 15 ml of 2M H_2SO_4/1M KBr and 10 ml of air. After 14-20 days at ambient temperature, the color of the solution was noted and the recovered electrocatalyst washed and weighed.

The results of the accelerated corrosion tests are shown in **Table 3-VI**. There is a consistent increase in stability with an increase in heat-treatment temperature as expected since the rate of corrosion for a given mass is highly dependent on the surface area. The blue and green colors are probably soluble bromide complexes of Pt and the alloying metal. Analysis by spectrophotometry on -4 sample solution showed a probable metal complex absorbance of 540 nm, and an absorbance around 340 nm, which is likely Br_3^- absorption. The red coloration is likely due to bromine that is generated by a catalyzed air oxidation of bromide ion. Titration with thiosulfate indicated a Br_2 concentration of 0.3 mM.

Due to the low precious metal contents of the G86-1-9 and G86-1-10 electrocatalysts, corrosion testing was conducted in a slightly different manner. Electrodes, with and without the Nafion coating, were immersed in the KBr/H_2SO_4 mixture. After removal of the electrodes, the solutions were analyzed for precious metal content. The general findings were as follows: The presence of the Nafion coating inhibited, but did not completely prevent, dissolution of the platinum; larger quantities of platinum (-50 mg/L) were found in solutions which contained the non-impregnated electrodes as opposed to the impregnated electrodes (-20 mg/L). The Nafion coatings did not appear to have any effect on the alloying component, with quantities

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from 6 to 9 mg/L found in all solutions. Significant corrosion of all electrocatalysts was observed. However, the G86-1-9 electrocatalyst can easily be protected by maintaining the electrode at hydrogen potentials; corrosion of the G86-1-10 electrocatalyst is still expected to occur (See Section 5.3.2) at hydrogen potentials.

TABLE 3-VI

ACCELERATED CORROSION TESTING EXPERIMENTS
(Solution Color and Catalyst Recovery)

Catalyst	Heat-Treatment				
	Untreated	500°C	700°C	900°C	1100°C
Pt Black	Lt. Green 64%	NT	NT	NT	NT
G86-1-2B	Brown 66%	Lt. Green 86%	Lt. Blue 90%	Lt. Blue 85%	Colorless 81%
G86-1-3	Reddish-Brown 48%	Lt. Blue 91%	V.Lt. Blue 92%	V.Lt. Blue 88%	
G86-1-4	Dk. Brown 70%	NT	NT	NT	NT
G86-1-5	Lt. Brown 80%	NT	NT	NT	NT
G86-1-6	Lt. Green 57%	Gr/Yellow 80%	Lt. Green 93%	--	--
G86-1-7	Dk. Orange 51%	Orange 85%	Green/Orange 100%	--	--
G86-1-8	Dk. Orange 38%	Blue/Green 88%	Lt. Green 89%	--	--

Dk.   = dark
Lt.   = light
V.Lt. = very light
NT   = not tested

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3.4 Conclusions

Experiments performed previously under NASA Contract NAS-24394 demonstrated that a non-heat-treated platinum alloy had improved tolerance to the presence of bromide ion as compared to platinum black. Data obtained in the present program, especially the floating electrode half-cell and cyclic voltammetry results, are also suggesting that a non-heat-treated, or a low-temperature heat-treated platinum-rich electrocatalyst yields the best response and minimum polarization losses in the presence of bromide ion. As demonstrated in Table 3-VI, heat-treatment of the platinum alloy improves its resistance to corrosion as evidenced by the higher percent recoveries. Corrosion of the hydrogen electrocatalyst is not expected to be a significant problem, since it can be overcome by maintaining the hydrogen electrode in a hydrogen environment, or, at the very least, by preventing the electrode from reaching an anodic potential where dissolution could occur.

Although it could not be confirmed visually with SEM analysis except for the 900°C heat-treated samples, for a given electrocatalyst composition, the surface area decreased as the heat-treatment temperature increased, due to sintering of the electrocatalyst particles. The larger particle size appears to have less tolerance to the presence of bromide ion, although the reasons for this are unknown at this time. This loss in surface area is also giving rise to increased polarization losses, even in the absence of bromide ion.

The results obtained in the hydrogen electrocatalyst evaluation are qualitatively in agreement with those observed previously. That is, a low temperature or non-heat-treated platinum rich alloy yields the best performance. Based on floating half-cell and cyclic voltam-

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metry results, the non-heat-treated G86-1-2 and G86-1-6, and the 500°C heat-treated G86-1-6 electrocatalysts were selected for full cell evaluation. Due to performance comparable to electrocatalysts containing an order of magnitude increased precious metal content, the G86-1-9 and G86-1-10 electrocatalysts were also selected for full cell evaluation.

3.5 References for Section 3.0

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4.0 BROMINE ELECTROCATALYST OPTIMIZATION

The objective of this portion of the program was to prepare and evaluate electrocatalysts for the liquid side of a H_2/Br_2 battery which would experience minimal intercalation of Br_2, yet have high electrocatalytic activity. Intercalation of bromine may cause long-term degradation of carbon catalysts, limiting the life of electrodes. During Phase I of this program, Black Pearls 2000 (BP2000), a high surface area carbon black manufactured by Cabot Corp., was identified as baseline Br_2 catalyst due to its anticipated low susceptibility to intercalation and its high activity. Potential methods of increasing resistance to Br_2 intercalation while maintaining high catalytic activity such as depositing a glassy carbon or pyrolytic carbon coating on BP2000 were also identified. In the Phase II program, nine types of BP2000 coated catalysts were prepared and evaluated for extent of Br_2 intercalation and catalytic activity.

When graphite is exposed to Br_2 an intercalation compound, generally C_7Br, is readily formed, causing the graphite lattice structure to expand. However, when the intercalation compound is no longer exposed to Br_2, the Br_2 partially desorbs, causing contraction of the graphite lattice structure. This expansion/contraction during intercalation/desorption may cause the lattice structure to fracture. During operation of a H_2/Br_2 battery, the liquid side catalyst will be subjected to repeated intercalation/desorption cycles as the battery is cycled between the charge and discharge modes. Long-term degradation of the Br_2 electrocatalyst may occur due to fracture of the carbon particles caused by this repeated cycling.

Electrode degradation will be minimized by using carbons which have low susceptibility to intercalation; these are carbons which have

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amorphous or random structures, rather than a layered graphitic structure. Since bromine intercalation occurs mainly along graphite basal planes (1), intercalation is minimized in carbons with a low basal plane to edge plane ratio. This occurs in very small particle size carbon blacks with turbostatic structures, such as BP2000. Another method of minimizing intercalation is to block graphite basal planes with a glassy carbon or pyrolytic carbon (epitaxial, but not graphitic) coating. However, it is difficult to prepare glassy carbons or pyrolytic carbons in the high surface area form required for catalytic activity.

In this program, samples of BP2000 with glassy and pyrolytic carbon coating were prepared and evaluated for intercalation resistance and catalytic activity. It was hoped that these catalysts would combine the inherent resistance to intercalation of BP2000 with the added intercalation resistance of the coating, while maintaining a relatively high surface area, thus providing a bromine electrocatalyst with longer life and high catalytic activity.

4.1 Bromine Catalyst Preparation

A total of nine glassy carbon and pyrolytic carbon coated BP2000 catalysts were prepared. These catalysts are designated G86-1-B1 through G86-1-B9; the designations are identified in **Table 4-I**.

TABLE 4-I

BROMINE ELECTROCATALYST DESIGNATION

Designation	Composition
G86-1-B1	BP2000 impregnated with 5 wt% phenolic
G86-1-B2	BP2000 impregnated with 10 wt% phenolic
G86-1-B3	BP2000 impregnated with 5 wt% polyvinylidene chloride
G86-1-B4	BP2000 impregnated with 10 wt% polyvinylidene chloride
G86-1-B5	BP2000 impregnated with 50 wt% phenolic
G86-1-B6	BP2000 impregnated with 1 wt% phenolic
G86-1-B7	BP2000, short duration, high flow rate, pyrolytic coating
G86-1-B8	BP2000, long duration, low flow rate, pyrolytic coating
G86-1-B9	BP2000, long duration, high flow rate, pyrolytic coating

4.1.1 Glassy Carbon-Coated Black Pearls 2000

Glassy carbons are produced by progressive coalescence of stabilized polymer chains at temperatures in the range 400-1000°C. The coalescence process produces a non-graphitic carbon with a highly chainy, ribbon-like structure. The development of a parallel stacked graphite structure is prevented because of strong continuity along the length of the ribbon.

In this program, glassy carbon coated BP2000 catalysts were prepared by impregnating BP2000 with a non-graphitizable polymeric resin solution, followed by heat treatment in an inert atmosphere at 700-900°C to decompose the polymer and form the glassy carbon. Six variations of glassy carbon coated BP2000 were prepared by varying the type (phenolic resin or polyvinylidene chloride resin), and concentration, 1-50 wt%, of the polymeric solution.

The basic heat-treatment procedure for the glassy carbon catalysts was to heat them at 900°C for 1-2 hours in an inert atmosphere. However, for several catalysts, this procedure was varied to determine the effects of heat-treatment on catalyst properties. The -B2 catalyst was divided into two batches for heat-treatment; the first batch

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underwent the standard procedure, while the second batch was initially heated at 350°C for one hour, then the temperature was slowly raised at ≈10°/min to 900°C, where it was held for one hour. The purpose of this procedure was to determine if the rate of heating, especially near the initial polymer decomposition temperature (350°C), affects the properties of the coating. The -B4 catalyst was also split into two batches to determine if heat -treatment at 700°C versus 900°C affects the catalyst properties or performance.

To determine if we were successful at coating the BP2000, samples of the -B1 and -B2 catalysts were examined by transmission electron microscopy (TEM). At the magnification used in the TEM, 600,000X, no significant differences in particle size or structure were observed between the coated materials and BP2000. However, as discussed in Section 4.2, the decrease in surface area of the glassy carbon coated BP2000 indicates that most of the attempts at coating BP2000 were successful.

4.1.2 Pyrolytic Carbon Coated Black Pearls 2000

Pyrolytic carbons are produced by the pyrolysis of gaseous hydrocarbons and subsequent deposition of solid carbon particles. Depositing carbon from hydrocarbons under pyrolyzing conditions is a common technique for producing carbon films or coatings, particularly for nuclear fuel. The structure and properties of pyrolytic carbons are highly variable and are dependent on the reaction conditions, including: type and concentration of the parent hydrocarbon, pyrolysis temperature, contact time, and the geometry of the pyrolyzing chamber (2).

In this program, pyrolytic carbon coatings were produced by introducing a mixture of 2% acetylene/argon to a horizontal rotating tube furnace containing BP2000; the furnace temperature was kept constant at 800-850°C, while the gas flow rate and the duration of the run were varied. A tube rotating at 30-40 rpm was used to provide mixing, and thus, hopefully produce a uniform coating. By varying the flow rate and run duration, three sets of coating conditions were used in the production of catalyst: 1) high flow rate, short duration, 2) low flow rate, long duration, and 3) high flow rate, long duration. Variations in flow rate and duration will affect the structure and extent of coating. A higher space velocity (flow rate) should yield smaller particles of the pyrolytic carbon, resulting in a high surface area, while a longer run duration should increase the amount of carbon deposited.

4.2 Bromine Catalyst Evaluation

The bromine electrocatalysts, including the six glassy carbon coated BP2000 preparations, the three pyrolytic carbon coated BP2000 preparations, and BP2000 itself, were evaluated for surface area, catalytic activity (half-cell performance), and resistance to bromine intercalation.

4.2.1 Surface Area

Surface areas of the bromine electrocatalysts were measured by two methods, BET N_2 adsorption and iodine number. For carbon blacks, these two methods are generally in agreement, although the iodine number may be influenced by the presence of volatile and extractable species, and by surface porosity.

In the BET method, a monolayer of N_2 molecules is adsorbed on the catalyst surface at the N_2 boiling point temperature. From the volume of N_2 adsorbed, and the knowledge of the area covered by a N_2 molecule at the adsorption conditions, the surface area of the sample can be readily calculated. In this program, a Micromeritics FlowSorb II surface area analyzer was used for all BET measurements.

The iodine adsorption numbers of the bromine electrocatalysts were determined using the American Society for Testing and Materials Standard D1510-85, with slight modifications to the specified reagent preparation procedures. As specified by the standard, a catalyst sample size of 0.125 g was used for the catalysts with I_2 numbers above 500 g/kg; that is, for all catalysts except -B5. For this catalyst, a 0.25 g sample was used. The BET surface areas and the iodine adsorption numbers for the bromine catalysts are listed in **Table 4-II**. For a given catalyst, there is generally good agreement between the iodine number and the BET surface area, particularly for the lower surface area materials. The slight discrepancy in the values for the high surface area materials is probably due to the high microporosity of these materials. Due to their small size, many of the micropores allow N_2 to enter but exclude iodine, causing the BET surface area to be larger than the iodine number.

There was a larger than expected discrepancy between the iodine number, 1138 g/kg, and the BET surface area, 1440 m^2/g, for the -B3 catalyst. The difference here was probably due to uneven coating of the BP2000 during the preparation of this catalyst. The sample of this catalyst used for the BET measurement was probably uncoated; its surface area was determined to be approximately the same as the surface area of BP2000.

TABLE 4-II

COMPARISON OF BET SURFACE AREA AND IODINE ADSORPTION NUMBER OF BROMINE ELECTROCATALYSTS

Bromine Electrocatalyst	Heat-Treatment	BET Surface Area (m²/g)	Iodine Adsorption No. (g/kg)
BP 2000	NONE	1430	1206
G86-1-B1	900°C/N_2/2 hours	1050	1038
G86-1-B2	900°C/N_2/2 hours	861	993
G86-1-B2	350°C/1 hour; 900°C/N_2/2 hours	849	880
G86-1-B3	900°C/N_2/1 hour	1440	1138
G86-1-B4	900°C/N_2/1 hour	1364	1145
G86-1-B4	700°C/N_2/1 hour	1359	1169
G86-1-B5	350°C/1 hour; 900°C/N_2/1 hour	371	324
G86-1-B6	900°C/N_2	1392	1162
G86-1-B7	NONE	1397	1202
G86-1-B8	NONE	852	883
G86-1-B9	NONE	948	1097

With exception of the -B3 catalyst, the iodine numbers and the BET surface areas for the bromine catalysts were lower than that of the starting BP2000, suggesting that we were successful in coating the BP2000. However, the coating of the -B6, a glassy carbon prepared from a 1 wt% phenolic precursor, and the -B7, a pyrolytic carbon prepared with a high acetylene flow rate, appear to be minimal. For both of these catalysts, the iodine numbers and BET surface areas were only slightly lower than those of BP2000. As expected, the catalyst with the lowest surface area was the -B5, a glassy carbon prepared from a 50 wt% phenolic precursor.

For the glassy carbon coated catalysts, little effect of heat-treatment procedure on surface area was noted. Although there was some difference in the iodine numbers of the -B2 heat-treated at 900°C and -B2 heat-treated at 350/900°C, the BET surface areas of these catalysts are similar. For the -B4 catalysts heat-treated at 700°C and heat-treated at 900°C, both the BET surface areas and the iodine numbers of the two samples are very similar.

4.2.2 Electrochemical Half-Cell Performance

The bromine electrocatalysts were evaluated for catalytic activity in a three-electrode half-cell configuration. In the test configuration, an iridium contact wire held the working electrode completely immersed in the Br_2/HBr electrolyte; a carbon felt counter electrode and Ag/AgBr reference electrode were also used. For these tests, the electrocatalysts were fabricated into electrodes containing 30% PTFE and supported on carbon fiber paper.

Charge and discharge polarization curves were obtained for each electrode in stirred solutions of 0.05M Br_2/8.2M HBr, simulating approximately zero percent state-of-charge (SOC) and 1.8M Br_2/4.6M HBr, simulating approximately 50% SOC. In the charge mode, the maximum current density was arbitrarily limited to 1,000 mA/cm^2 for both solutions. In the discharge mode, the maximum current density attainable in the first solution was only 80-100 mA/cm^2, due to the low bromine concentration present. In the second solution, discharge current densities of 800-1000 mA/cm^2 were attainable, due to the higher Br_2 concentration. Duplicate tests using fresh electrodes were performed for all of the catalysts.

In the half-cell testing, no significant differences in catalyst

performance were noted in either solution. The polarizations at a given current density in a given solution were similar for all of the catalysts, including BP2000. Thus, the performance of the catalyst appears to be independent of surface area, at least over the range tested, 371 m^2/g (-B5) to 1430 m^2/g (BP2000). Typical polarization curves for the -zero percent SOC and the -50% SOC solutions are shown in **Figures 4-1** and **4-2**, respectively. In these figures, the data are plotted in terms of overpotential, defined as the differences between the observed voltage and the open circuit voltage, as a function of current density.

A slight increase in average overpotential in the charge mode was noted as the HBr solution concentration decreased from 8.2M in the first solution to 4.6M in the second solution. This increase, due to concentration polarization, was expected.

4.2.3 Intercalation Testing

The resistance of the catalysts to intercalation of bromine was evaluated by three different methods. The tests were designed to accelerate intercalation by exposing the catalysts to high bromine concentrations for 20-100 hours. Despite the accelerated nature of the tests, no conclusive evidence of bromine intercalation or of catalyst degradation due to intercalation was noted for any of the catalysts.

In the first intercalation testing method, samples of BP2000 and five glassy carbon coated BP2000 catalysts were mixed with a solution of 60% HBr (8.8M) and 40% Br$_2$, and held at 60°C in a vacuum desiccator for 100 hours. The samples were subsequently cooled and washed thoroughly with distilled water until all of the Br$_3^-$ color disappeared
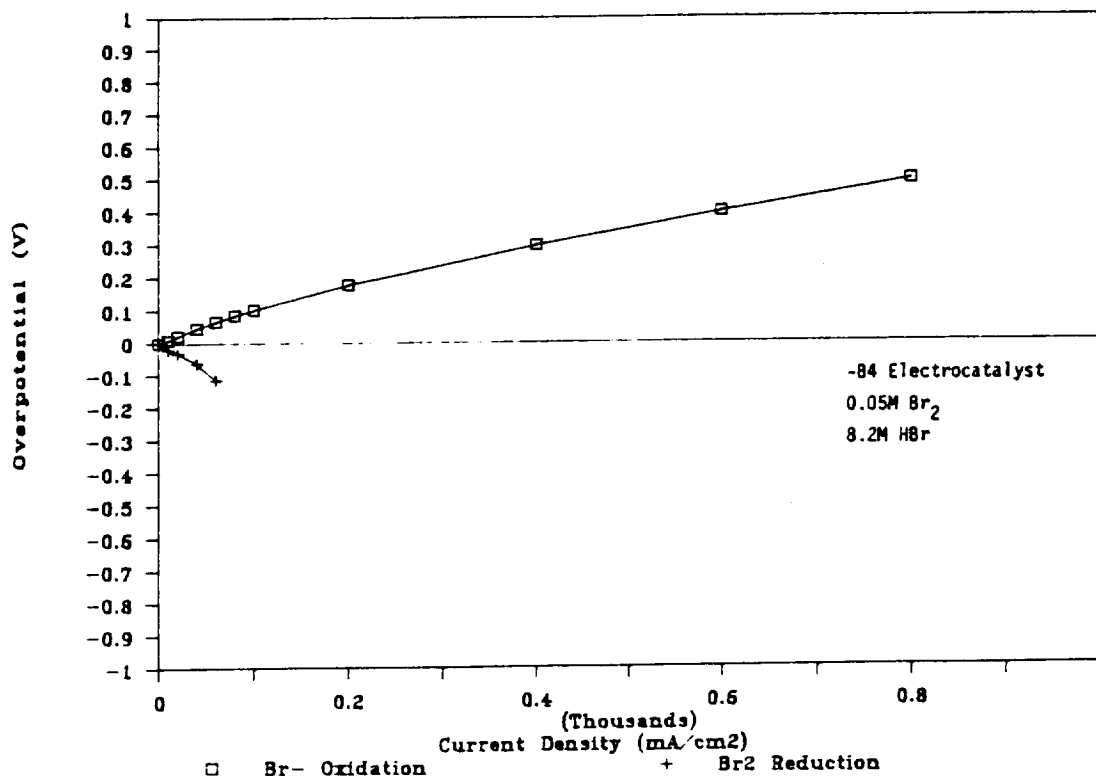
33

Figure 4-1. Typical Polarization Curve for Br_2 Catalyst in 0.05M Br_2/8.2M HBr
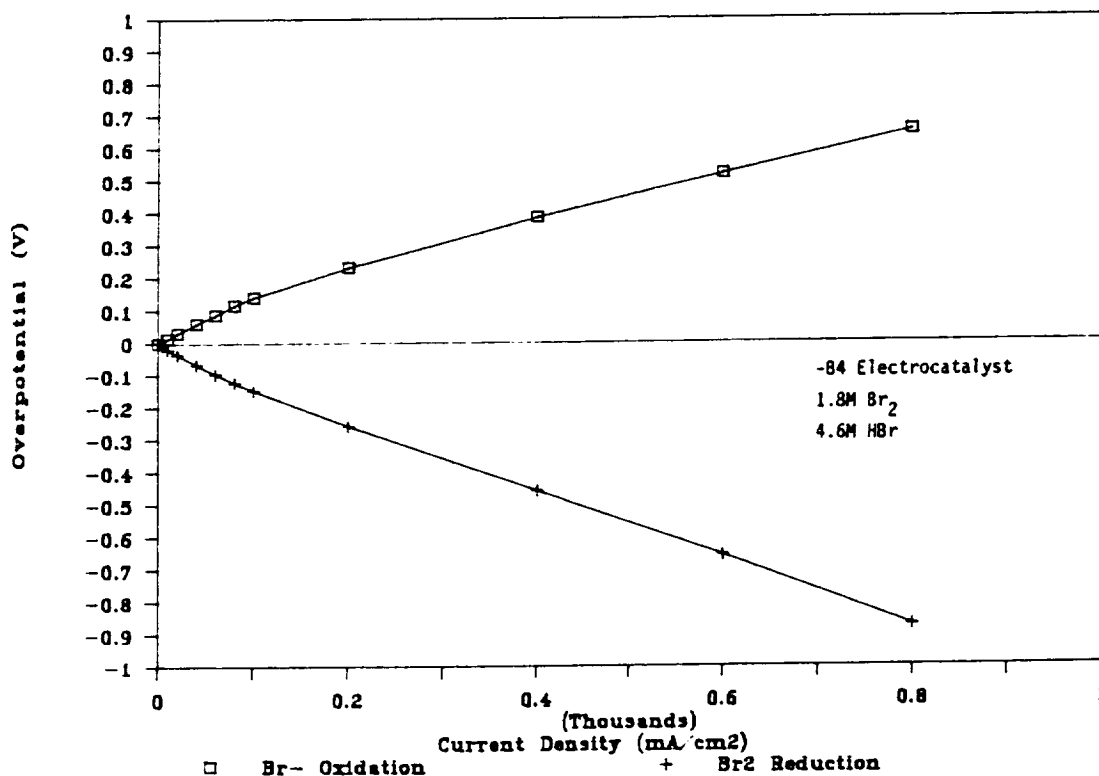

Figure 4-2. Typical Polarization Curve for Br_2 Catalyst in 1.8M Br_2/4.6M HBr

from the wash water. An ultrasonic bath was used in a final washing step. The samples were then dried and analyzed by X-ray diffraction. The diffraction patterns of the post-test samples were compared with spectra of catalyst samples not exposed to HBr/Br_2 to determine if the lattice spacing had changed, which could then be attributed to Br_2 intercalation.

The diffraction patterns of the catalyst samples exposed to bromine were very similar to those of the non-exposed samples, except for an increased background response in the bromine exposed samples over the entire range of angles scanned. The cause of the increased background is not known; perhaps some liquid bromine still remained in the samples and caused the interference.

In all other aspects, the diffraction patterns of the pre- and post test samples were very similar, with no evident changes in the lattice parameters. However, BP2000 has a very broad spectrum, due to its highly amorphous nature and very small particle size (~200 Å), so detecting changes in its spectrum is difficult. The same is true of the glassy carbon-coated BP2000 samples, which have spectra very similar to that of BP2000. From the broad diffraction spectra produced by these samples, no Br_2 intercalation was evident. Based on these results, the remaining catalysts were not tested by this method, and a second method was developed for evaluating intercalation resistance.

In the second intercalation test, samples of dried catalyst were carefully weighed and placed into a chamber at room temperature, where they were exposed to a Br_2 saturated N_2 stream for 24 hours. The chamber was then purged with N_2 for two hours, and the sample weights were recorded. Next, the bromine containing samples were heated at

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60°C for one hour, then at 200°C for one hour, to drive off the bromine. Sample weights were recorded after both heating steps. The net weight gain after exposure to Br_2 and the subsequent weight loss during heating may be an indication of the extent of Br_2 intercalation. A similar technique, using a thermogravimetric analyzer to record weight loss as a function of temperature, has been used by other investigators to study Br_2 intercalation in graphite (3).

All of the bromine electrocatalysts, including BP2000, were evaluated for resistance to intercalation by this method. In addition, samples of 2700°C heat-treated Vulcan XC-72 (HTV, Cabot Corp.) and 2700°C heat-treated BP2000 (HTBP), were evaluated. These materials, with surface areas of 60 m^2/g and 180 m^2/g, respectively, have graphite structures and would be expected to undergo Br_2 intercalation. In Phase I of this program, Br_2 intercalation of HTV was confirmed by X-ray diffraction.

The results of this test were inconclusive. As shown in **Table 4-III**, the trend in the data is for the weight gains during exposure to Br_2 and subsequent weight loss during heating (combined 60°C and 200°C steps), to increase as the catalyst surface area (BET) increases. Thus, the HTV and HTBP samples, with the lowest surface areas, have the lowest weight gains after Br_2 exposure, while BP2000 with a high surface area, has a high weight gain. However, the HTV and HTBP samples are graphitic, and would be expected to intercalate as evidenced by the Phase I X-ray data, while BP2000 has an amorphous structure and would not be expected to intercalate. This raises the question of whether the weight gain of the catalyst samples following exposure to Br_2 is due to the formation of intercalation compounds or to surface physical adsorption, or to a combination of both. The

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amount of Br_2 adsorbed on the catalyst surface would be expected to increase as the surface area increases, while intercalation is expected to be greatest for the most graphitic materials, in this case the catalysts with the lowest surface areas.

TABLE 4-III

BROMINE VAPOR INTERCALATION OF CARBON CATALYSTS

Catalyst	BET Sample Analysis (m^2/g)	Weight Gain (%) After 24 hr Br_2 Exposure	Weight Loss (%) After Heating 60°C + 200°C	Weight Loss at 60°C as % of Total Loss
HTV	≈60	4.9	10	9
HTBP200	180	7.1	6.0	19
Vulcan	≈250	15.3	6.9	29
-B5	371	45	25	16
-B4 HT 900°C	1363	64.1	36.1	34
-B2 HT 900°C	861	71.6	39.4	47
-B8	852	77.4	30.4	39
-B1	1050	82.6	37.6	41
-B9	948	84.4	33.2	42
-B2 HT 350°/900°C	849	97.6	42.4	48
-B4 HT 700°C	1359	102.4	47.7	40
BP2000	1430	108.8	43.1	63
-B7	1397	110.8	50.7	52
-B6	1392	115.8	51.6	50

One method of possibly distinguishing between surface adsorption of Br_2 and intercalation of Br_2 was to measure the weight loss following 60°C heat-treatment and compare this to the weight loss following 200°C heat-treatment. Although saturated bromine intercalation compounds will lose bromine at room temperature as soon as they are removed from the Br_2 atmosphere, the bulk of the bromine desorbs above a critical temperature at which exfoliation occurs, which is dependent on the concentration of the intercalate, and ranges from 80°C for concentrated compounds to 150-170°C for dilute compounds (3).

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It was felt that Br_2 physically adsorbed on the surface would desorb at lower temperatures than the intercalate, so 60°C, slightly above the Br_2 boiling point, was chosen. This weight loss data, expressed as the Br_2 weight loss at 60°C as a percentage of the total weight loss at 60°C and 200°C, is also included in Table 4-III. Although there is some scatter, the data tend to indicate a lower percentage of Br_2 loss at 60°C in the graphitic samples, for example, 9% for HTV, and higher percentage of total Br_2 loss at 60°C for BP2000 (63%), and the coated catalysts. This is not strong evidence of Br_2 intercalation in the graphitic controls or Br_2 adsorption on the high surface area catalysts, but it provides some explanation for the weight gain data trend.

In the third method for determining the resistance of catalysts to intercalation, selected bromine electrodes were evaluated for changes in electrode thickness, weight and structure following 20 hours of Br_2 evolution at the electrode surface. The electrodes, containing 30% PTFE and supported on carbon fiber paper, were placed in a well-stirred 5M HBr solution and held for 20 hours at a fixed potential at which the Br^- oxidation current density was 300-500 mA/cm². At this current density, Br_2 evolution at the electrode surface was vigorous. After the test, the electrodes were removed from the HBr/Br_2 solution, air dried for 2 hours to allow liquid HBr/Br_2 to evaporate from the electrode surface, then weighed and examined for changes in thickness and structure with a 5X microscope.

Electrocatalysts tested by this method included BP2000, selected glassy carbon-coated BP2000 and pyrolytic carbon-coated BP2000 catalysts, and HTV, to serve as a graphitic control. None of the electrodes tested had significant changes in electrode thickness or

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structure. Typically, small weight gains of 3-6% were noted for the electrodes following removal from the HBr/Br$_2$ solution and 2 hours of air-drying. However, in a few runs, high weight gains of 23-38% were noted. The electrode weight gain did not appear to be a function of electrode surface area or of the oxidation current density at which the electrode was held. The high weight gains may be due to liquid HBr/Br$_2$ remaining on the electrode surface or to moisture pickup from the air.

The generally small weight gain and the stability of the electrode thickness and structure following Br$_2$ evolution from the electrode surface tend to indicate that no significant intercalation of bromine in the electrode structure occurred. However, although this test was accelerated by holding the electrodes at a high oxidation current for 20 hours, it is not necessarily indicative of electrode intercalation and stability over many battery discharge/charge cycles.

4.3 Bromine Catalyst Selection

No significant differences in either catalytic activity or resistance to Br$_2$ intercalation were noted among the ten bromine electrocatalysts tested. Placing a glassy carbon or pyrolytic carbon coating on BP2000 did not significantly decrease catalytic activity, or improve resistance to intercalation, at least as determined by the testing methods used in this program. Since BP2000 exhibited good resistance to intercalation and also no significant advantages to using the coated catalysts were shown, BP2000 was chosen as the bromine catalyst for all of the full cell tests, described in Section 5.0. This catalyst has been shown to have a high catalytic activity for both Br$^-$ oxidation and Br$_2$ reduction, and to be resistant

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to Br_2 intercalation due to its very small particle size and amorphous structure. It is also economical, readily available, and does not require any further processing steps as do the glassy carbon and pyrolytic carbon coated catalysts. Thus, BP2000 is the recommended bromine electrocatalyst.

4.4 References for Section 4.0

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5.0 FULL CELL EVALUATION

5.1 Introduction

Full cell testing of the hydrogen-bromine battery was carried out to evaluate various components/configurations of the system. All testing was conducted in subscale (2"x2" active area) hardware. Parameters investigated included: a) effect of electrode structure, b) effect of electrocatalyst and c) type of solid polymer electrolyte membrane. Full cell testing consisted mainly of electrode performance evaluation by running charge and discharge polarization curves in HBr concentrations corresponding to 42 and 85% state-of-charge (SOC). As a measure of the electrical efficiency of the battery, the discharge voltage/charge voltage ratio at 200 mA/cm^2 was calculated. All testing was conducted at room temperature.

5.2 Experimental

An exploded view of the hydrogen-bromine battery is shown in **Figure 5-1**; this particular view is of a one component membrane/electrode assembly (MEA). Not visible is the piece of carbon felt used to direct liquid flow up to the bromine electrode assembly.

The full cell test facility is shown schematically in **Figure 5-2**. Liquid flow rate through the cell was controlled by use of valves V-2 and V-3. During the course of the program, a surge tank containing a reference electrode assembly was placed in between the pump and the flowmeter; this is not shown in Figure 5-2.
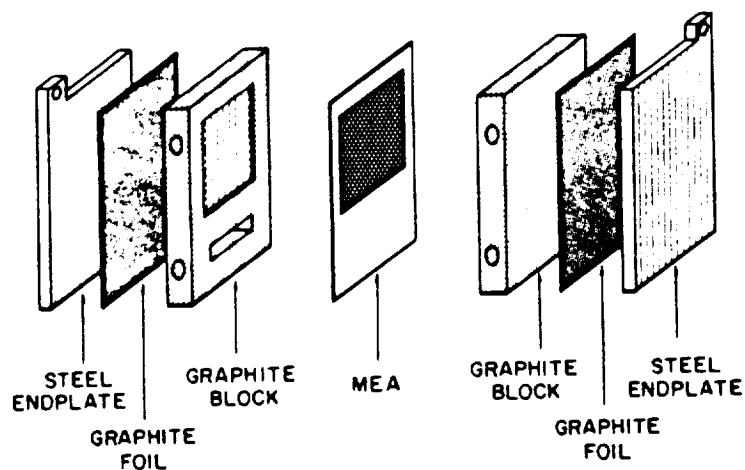
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STEEL ENDPLATE · GRAPHITE BLOCK · GRAPHITE FOIL · MEA · GRAPHITE BLOCK · GRAPHITE FOIL · STEEL ENDPLATE

Figure 5-1. Exploded View, Hydrogen/Bromine Battery

WATER RESERVOIR · FUME EXHAUST · V-1 · LIQUID SEAL · FROM GAS PANEL · CELL · H₂Br₂ · FLOWMETER · V-3 · Br₂/HBr RESERVIOR · V-2 · TO DRAIN · PUMP

⋈ VALVE
⊖,⊕ SHUT-OFF VALVE
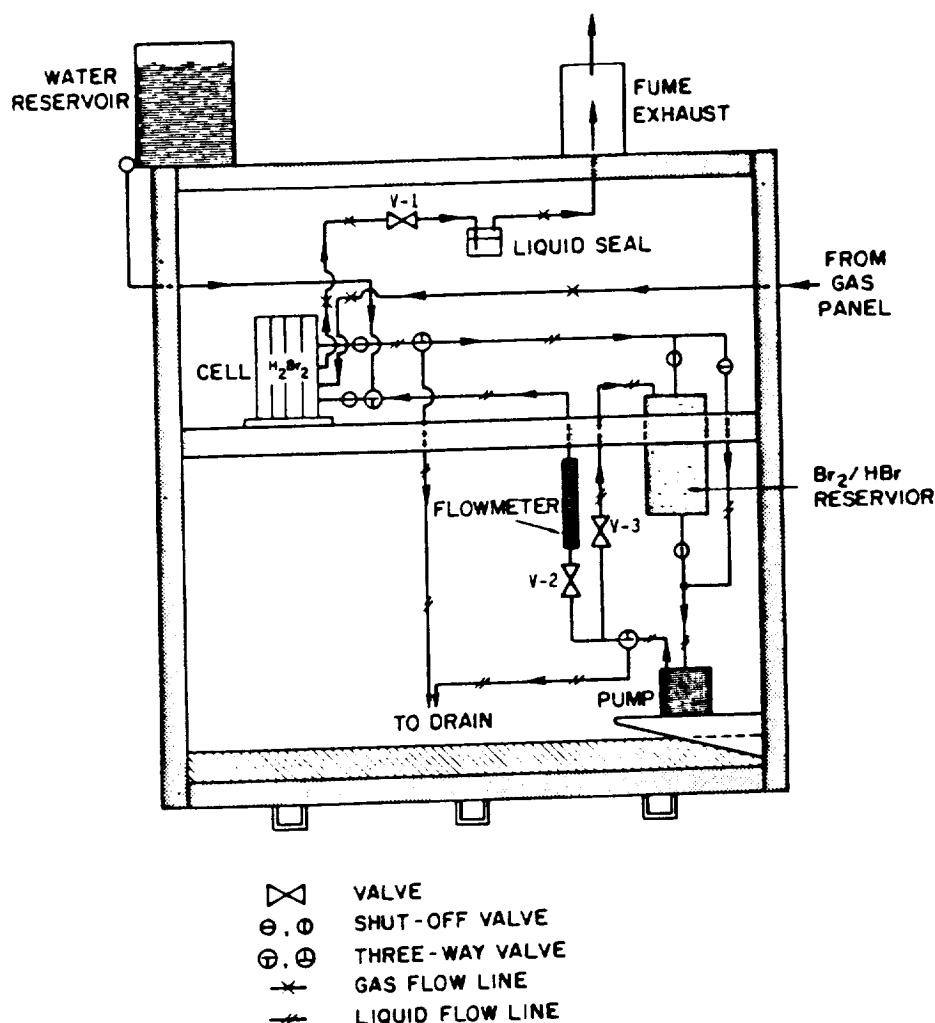⊕,⊕ THREE-WAY VALVE
⤬ GAS FLOW LINE
⤙ LIQUID FLOW LINE

Figure 5-2. Hydrogen/Bromine Battery Test Stand

The hydrogen pressure and therefore the cell pressure were typically set at 5 psig by a regulator external to the test stand; the pressure drop to atmospheric pressure was across Valve V-1. Hydrogen flow rates were established by opening Valve V-1 and visually monitoring the rate of bubbling in the liquid seal. Typically the bubbling rates were kept to 4-5 bubbles per minute. Several experiments were conducted using 10 psig hydrogen pressure, with no noticeable effect on performance. The majority of the experiments were conducted using dry hydrogen. However, several tests were performed studying the effect of humidified hydrogen for various hydrogen electrode structures. Humidification was implemented by bubbling the hydrogen through distilled water, using a gas dispersion tube.

The cell current and voltage waveforms were controlled by means of an automatic sequencer. Use of the apparatus allowed automatic switching between the charge and discharge modes of operation. A power supply was used to drive the battery in the charge mode of operation; the same power supply was used as a load during discharge. Charge and discharge times could be varied independently. A two-pen strip chart recorder was used to monitor both current and voltage, while a two channel electronic integrator independently measured the number of coulombs passed in both the charge and discharge modes of operation.

5.3 Results

5.3.1 Electrode Structure Development

Initial full cell testing was conducted using a three component electrode structure in which free standing hydrogen and bromine electrodes were against, but not bonded to, the membrane.

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Concurrent with the change to a bonded electrode structure was a change in the bromine electrode configuration. Initial bromine electrodes evaluated consisted of Black Pearls 2000 (BP2000) catalyst, supported on thin (2-3 mil) carbon fiber paper (CFP). This structure was modified to include a piece of carbon felt in the flow field, to force more liquid to the active electrode area, thus improving mass transport and HBr concentration management. Next, the active electrode area was moved away from the solid polymer electrolyte membrane, to minimize contact between bromine and the membrane.

The improvement in performance when going from free-standing (Build 4) to bonded electrodes plus the addition of carbon felt to the flow field (Build 6) is summarized in **Table 5-I**. An increase in discharge voltage, along with a tremendous decrease in charge voltage, was observed; bromine and HBr concentrations were about the same for the two runs. Measured cell resistances were the same, so the increase in performance was partially attributed to improved flow through the bromine electrode structure.

TABLE 5-I

IMPROVEMENTS DUE TO BONDED, FLOW-THROUGH ELECTRODE

Build No.	Electrode Configuration	Discharge (mV)	Charge (mV)	Ratio	OCV (mV)
4	Free-Standing, Flow-By	786	1830	0.43	1009
6	Bonded, Flow-Through	839	1351	0.62	1027

Build 5, identical in configuration to Build 4, could not obtain 200 mA/cm^2 in the charge mode. However, Build 5 was the first to contain a reference electrode so that individual electrode polarizations could be measured. Examination of the individual electrodes showed lower polarization for both electrodes in Build 6, demonstrating that bonding the hydrogen electrode to the membrane helped to improve the performance of this electrode.

Presently available commercial solid polymer electrolyte membranes do not completely exclude bromine species. Therefore, the approach that was taken to minimize bromine transport across the solid polymer electrolyte membrane, which will poison the hydrogen electrode, was to broaden or disperse the reaction zone on the *liquid* side. This will decrease localized high bromine (or HBr) concentrations at the membrane surface. Methods used to implement this technique included the use of a layer of "activated" carbon fiber paper and a layer of metal oxide bonded directly to the membrane on the liquid side (the metal oxide was located between the membrane and the BP2000 electrocatalyst). It was found that use of these methods resulted in no detectable change in the cell iR.

Results obtained using a layer of "activated" carbon fiber paper in the bromine electrode structures are summarized in **Table 5-II**, which compares Build 6 (plain carbon fiber paper) to Build 7 (activated carbon fiber paper). Using 2M HBr on the liquid side (which corresponds to -85% SOC), improvements were noted in both the charge and discharge modes with use of the activated layer. Another test using this configuration gave 74% electrical efficiency, the highest observed to that point in time. When 5M HBr was used on the liquid side (corresponding to -42% SOC), no change was observed in

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cell performance. The improved performance in the charge mode in 2M HBr solution, where the bromide ion concentration is relatively low, using the "activated" carbon fiber paper electrode structure, may be due to the electrode broadening effect of the "activated" carbon paper, providing a greater catalytic area and hence, more efficient electrode structure. In the 5M HBr solution, where the bromide ion concentration is high, the added catalytic area provided by the "activated" carbon paper is not required. Performance in the discharge mode is opposite of what was expected, and is not completely understood at this time.

TABLE 5-II

EFFECT OF ACTIVATED CARBON FIBER PAPER

Build No.	Carbon Fiber Paper	HBr Conc (M)	Discharge (mV)	Charge (mV)	Ratio	OCV (mV)
6 7	Plain Activated	2 2	839 873	1351 1233	0.62 0.71	1027 1018
6 7	Plain Activated	5 5	719 717	1079 1081	0.67 0.66	896 871

Due to the improved efficiency observed with the use of the layer of "activated" carbon fiber paper for at least part of the operating regime, this layer was incorporated into subsequent builds as a standard component.

The layer of metal oxide deposited on the membrane can also function as a bromine electrocatalyst. Therfore, a cell was fabricated with the metal oxide and "activated" carbon fiber paper, but without the BP2000. **Figure 5-3** shows the individual electrode polarizations

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for Build 9 (no BP2000 present) while **Figure 5-4** shows individual electrode polarizations of Build 7 (BP2000 present). In general, the polarizations for Build 9 are greater than those of Build 7 and the increased polarization of the Br_2 electrode, on charge, is the most significant difference. Therefore, use of the BP2000 electrocatalyst results in lower Br_2 evolution polarization. This is likely due to the high surface area BP2000 promoting the Br_2 evolution reaction.

Table 5-III summarizes full cell test data from Builds 9 and 7 in both 2 and 5M HBr; lower discharge and higher charge voltages were observed with Build 9 as compared to Build 7. The electrical efficiency for Build 9, (60%) is lower than that observed for Build 7, ($\geq$65%). Again, this was due to the use of the high surface area BP2000 in Build 7.

<center>

TABLE 5-III

FULL CELL PERFORMANCE IMPROVEMENT DUE TO BP2000

</center>

Build 7	2M HBr	5M HBr	Difference
Cell Voltage			
Open Circuit	1015	870	145
Discharge (200 mA/cm^2)	855	714	141
Charge (200 mA/cm^2)	1234	1101	133
Eff. (Disch/Charge), %	69	65	---

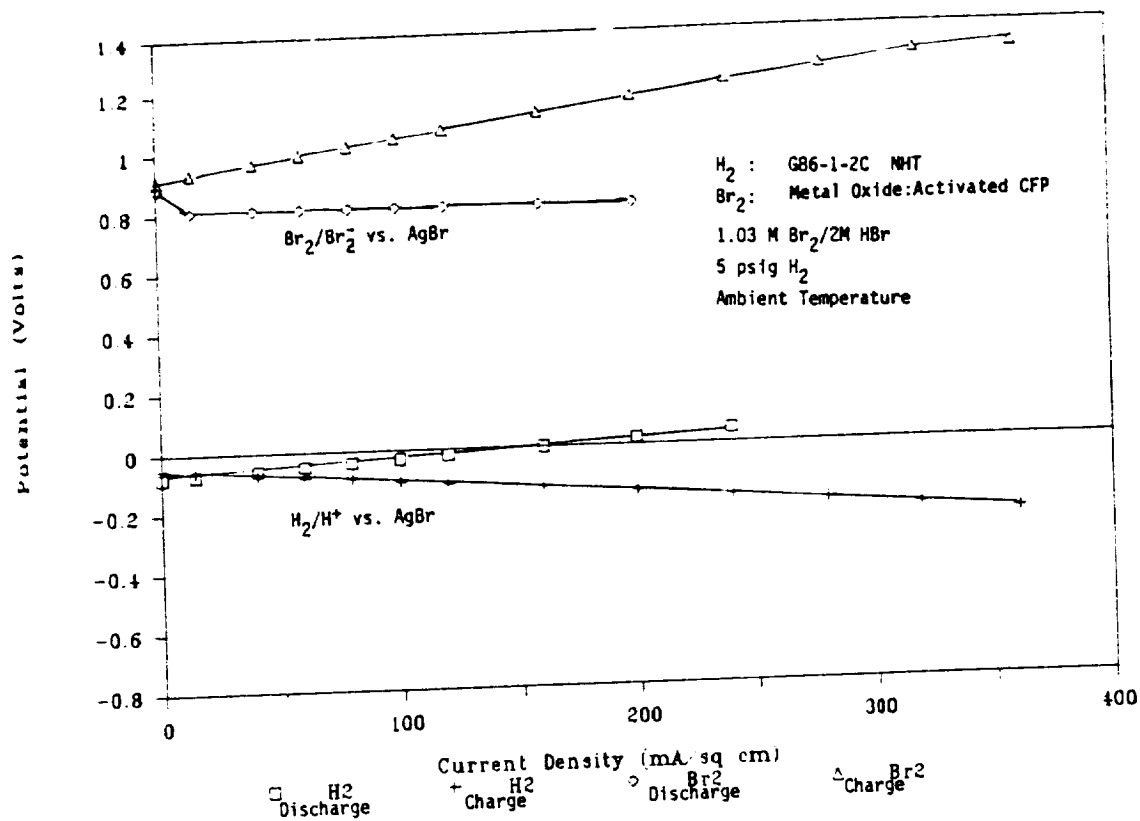| Build 9	2M HBr	5M HBr	Difference
Cell Voltage			
Open Circuit	967	870	97
Discharge (200 mA/cm^2)	788	706	82
Charge (200 mA/cm^2)	1322	1182	140
Eff. (Disch/Charge), %	60	60	---

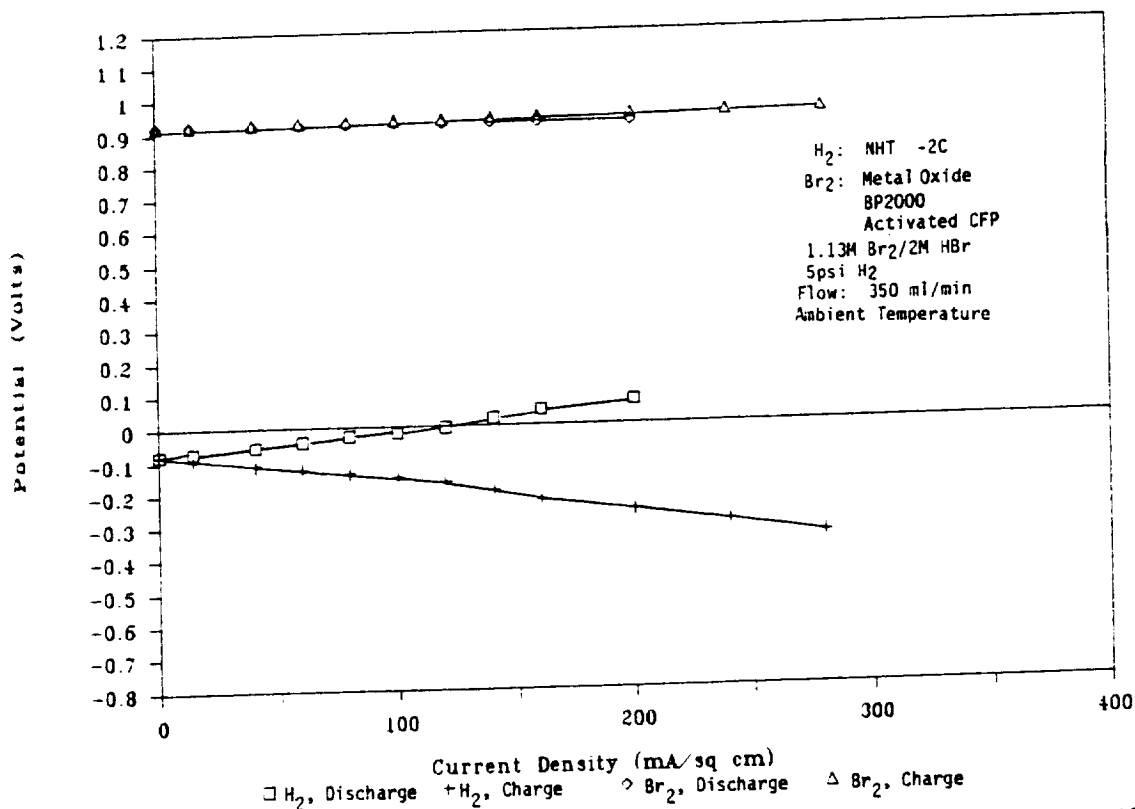Figure 5-3. Full Cell Polarization Scan in 2M HBr - Build #9, Scan #8 (H_2 & Br_2 vs. Ag/AgBr)

Figure 5-4. Full Cell Polarization Scan in 2M HBr - Build #7, Scan #3 (H_2 & Br_2 vs. Ag/AgBr)

A final test in this series was conducted depositing a thin layer (2 mg/cm^2) of BP2000 directly on the metal oxide surface. This loading was lighter than the 5 mg/cm^2 of BP2000 normally deposited on carbon fiber paper. Results are summarized in **Table 5-IV**, which compares the charge polarization and the discharge polarization at 200 mA/cm^2 for Build 7 (BP2000 on carbon fiber paper) Build 9 (no BP2000) and Build 11 (BP2000 on metal oxide). The largest polarizations were observed for the full cell which did not contain any BP2000. These tests indicate that BP2000 is a better electrocatalyst than metal oxide for the bromine reactions, particularly for bromide ion oxidation. However, BP2000 alone is difficult to bond to the Nafion membrane, while the metal oxide is readily bonded to the membrane. The metal oxide provides an intermediate low contact resistance interface to the membrane. The presence of the metal oxide layer on the membrane also prevents the Br$_2$/HBr liquid from directly contacting the membrane, an undesirable situation. Therefore, a composite bromine electrode structure consisting of metal oxide bonded to the membrane, followed by a free-standing BP2000 electrode, and a sheet of "activated" carbon fiber paper, was developed.

TABLE 5-IV

EFFECT OF BLACK PEARLS ON FULL CELL PERFORMANCE

	Build 7 (BP2000/Carbon Fiber Paper)	Build 9 (No BP2000)	Build 11 (BP2000/ Metal Oxide)
V(Charge: OCV) V(OCV: Discharge)	219 mV 160 mV	355 mV 179 mV	256 mV 152 mV

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The effect of using a carbon-supported noble metal alloy as a hydrogen electrode structure was investigated. This structure has the potential of lower noble metal loading and also ease of impregnation with an ionomer to achieve improved tolerance to bromine species. Typical solid polymer electrolyte fuel cells utilize noble metal catalysts at a loading of 4-6 mg/cm^2, while gas diffusion electrodes used in phosphoric acid fuel cells have noble metal loadings of 0.5 mg/cm^2 (dispersed on a carbon black support). Recent work at Los Alamos National Laboratories has demonstrated that the phosphoric acid fuel cell type gas diffusion electrodes can be used with a solid polymer electrolyte membrane if the electrode structure is impregnated with liquid Nafion to allow for hydrogen ion conduction (1). This technique was extended by us for use in a hydrogen-bromine fuel cell. **Table 5-V** summarizes results obtained using the supported electrocatalysts on the hydrogen electrode side (Build 12) and compares them to a full cell build which had a non-supported hydrogen electrode. Using a precious metal content of about 0.55 mg/cm^2, results were obtained which were comparable to those obtained in a cell which had a precious metal hydrogen electrode loading of about 7.5 mg/cm^2. **Figures 5-5** and **5-6** are the polarization scans for Build 7 (non-supported hydrogen electrocatalyst) and Build 12 (the supported electrocatalyst). These scans were obtained under the same conditions and are identical, demonstrating no loss in performance with a lowered precious metal content.
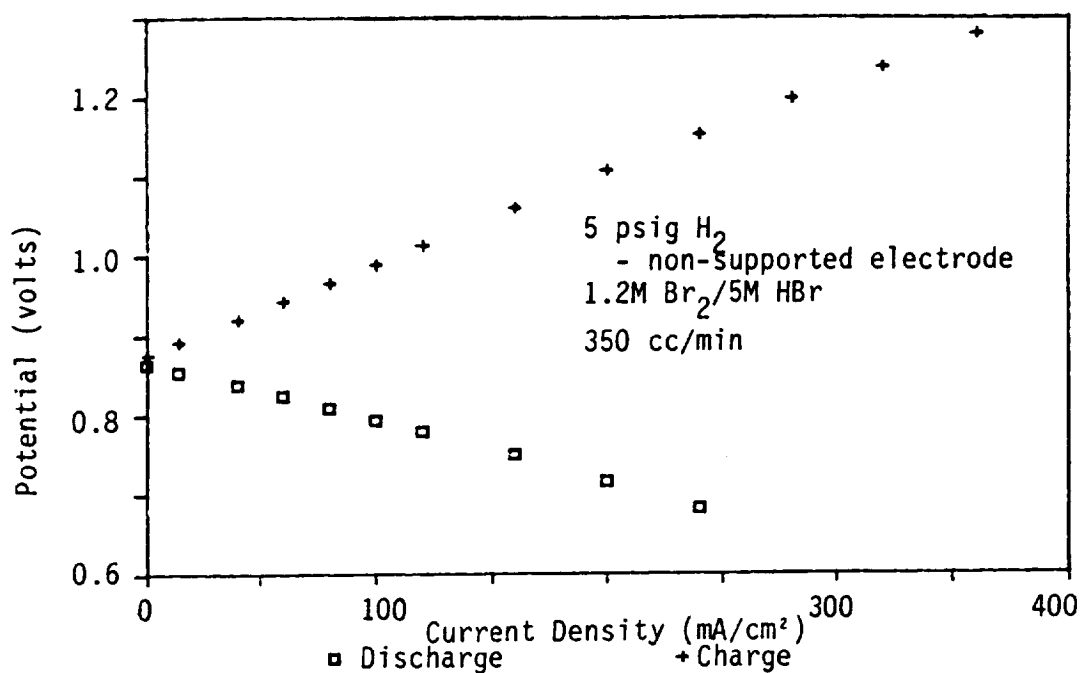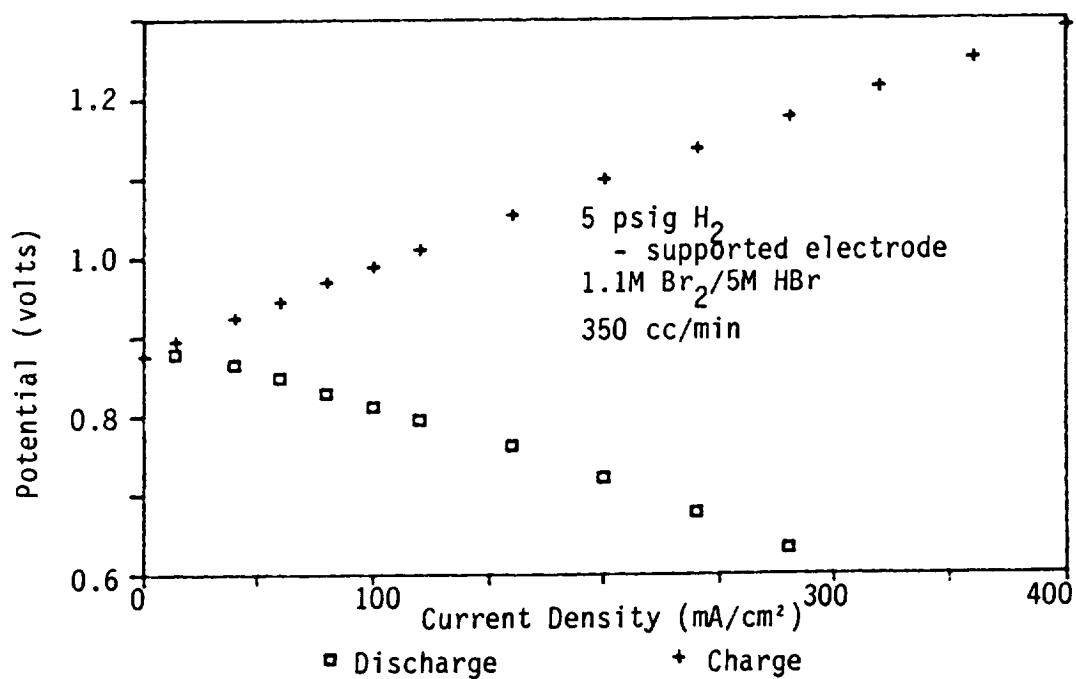
Figure 5-5. Build 7, Polarization Curves

Figure 5-6. Build 12, Polarization Curves

TABLE 5-V

EFFECT OF SUPPORTED HYDROGEN ELECTRODE
ON CELL VOLTAGE AT 200 mA/cm^2

Build No.	Hydrogen Electrode	Noble Metal Loading (mg/cm^2)	Discharge (mV)	Charge (mV)	Ratio	OCV (mV)
7	Non-Supported	7.5	714	1101	0.65	870
12	Supported	0.55	720	1092	0.66	881

The effect of humidifying the hydrogen inlet gas stream was also examined. Humidification was expected to improve cell performance by more effectively hydrating the hydrogen electrode/Nafion interface, especially when operating on dry gas in the discharge mode. In the discharge mode, humidification would also supply enough water to the cell to be osmotically pumped across the membrane and dilute the HBr which is formed at the membrane/bromine electrode interface.

Results obtained using humidified hydrogen are summarized in **Table 5-VI**. In Scan 6, an improvement in both charge and discharge performance was seen, up to 240 mA/cm^2, possibly indicating a beneficial effect. However, 280 mA/cm^2 could not be sustained on discharge, perhaps due to hydrogen electrode flooding. By increasing the flow rate of the humidified gas, a current density of 320 mA/cm^2 could be sustained. No change in performance was noted between the normal and increased hydrogen flow rate using dry hydrogen.

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In full cell tests, a unitized membrane assembly structure, in which the hydrogen and bromine electrodes were bonded to the solid polymer electrolyte membrane, provided the best performance. Cell performance was also enhanced by addition of a layer of "activated" carbon fiber paper to the bromine electrode structure. Using this electrode structure, electrical efficiencies, defined as the discharge voltage/charge voltage ratio at 200 mA/cm^2, as high as 78% were observed.

6.2 Recommendations for Future Work

Further research on the hydrogen-bromine battery should include long-term performance and stability testing of the catalysts and electrode structures. Although accelerated corrosion tests of the hydrogen electrocatalysts and accelerated intercalation tests of the bromine electrocatalysts were performed in this program, long term tests at actual operating conditions through many charge/discharge cycles are required to evaluate the stability of the catalysts and electrodes.

Evaluation of the hydrogen-bromine battery system has thus far been limited to single-cell testing, using a 2"x2" active-cell area. Scaleup to a multi-cell stack and larger active-cell area is required for complete battery evaluation.